The Study of the Structural Phase Transitions in ABCl$_3$ Single Crystals

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The birefringence of some ABCl$_3$ crystals in the phase transition regions was studied.
An analysis of the data is carried out within the Landau theory. Comparison of optical
data with those of heat capacity and elasticity is made. The coefficients of a thermo-
dynamical potential are determined. It is shown that the theory satisfactorily describes
the structural phase transitions in ABCl$_3$ crystals.

§1. Introduction

Over the last few years there has been a
growth of interest for the structural phase
transitions (PT) in ABX$_3$ crystals (A, B-cations,
X-halogen, oxygen). Among the oxide members
of this family there are some ferroelectrics which
are used as optoelectronic elements.[1] The
halide compounds undergo nonferroelectric
PTs. The study of such transitions (complicated
by the difficulties of PT parameter measure-
ments)[2] is important from the view point of
general problem on PTs. Some ABCl$_3$ crystals
are acousto-optic materials of interest.[3]

The temperature dependence of a PT param-
eter can be obtained from the birefringence
measurements.[4] It has been shown that the
birefringence of ABO$_3$ ferroelectrics is de-
termined by spontaneous electro-optic effect.[5]
It is worthwhile to carry out a systematic study
of the birefringence behaviour in ABX$_3$ crystals
and to compare the data with the Landau
theory.[6]

The measurements of the birefringence in
SrTiO$_3$,[7] KMnF$_3$,[4] CsPbCl$_3$[3,8] have led to the
conclusion that the critical index of a PT
parameter differs from the mean field value β
$=1/2$, but equals to about 1/3. Some authors
explain these discrepancies as a consequence of
the critical phenomena.[4,7,9]

§2. Experiment and Discussion

In the present paper the birefringence of some
ABCl$_3$ crystals in the PT regions was studied.
Except RbMnCl$_3$, all crystals under study
belong to the perovskite structure and undergo
the successive PTs $O_h^1 \rightarrow G_1 \rightarrow G_2 \rightarrow G_3$ (only O_h^1
$\rightarrow G_1$ PT in CsCaCl$_3$ was observed).[3] The

nature of these antiferrodistortive PTs is con-
nected with the instability of the cubic ABCl$_3$-
lattice in respect to soft modes at the boundary
points M and R of the Brillouin zone. Structure
of the crystals is slightly distorted as compared
with the ideal cubic structure. The distortions
are determined by the tilts of BCl$_6$ octahedra
about different axes of the initial cubic cell. The
tilt angle of BCl$_6$ tilts can be considered as a
thermodynamical PT parameter.[10]

The birefringence measurements were made
along the pseudocubic directions [100] by Berek
and Senarmont compensators with single
domain samples or on untwinned part of a
sample (Fig. 1).[3] The PT sequence of the first,
the second and the first order is observed. The
PT temperatures are shown in Table I.

The thermodynamical potential of the PTs in
halide ABX$_3$ perovskites was considered else-
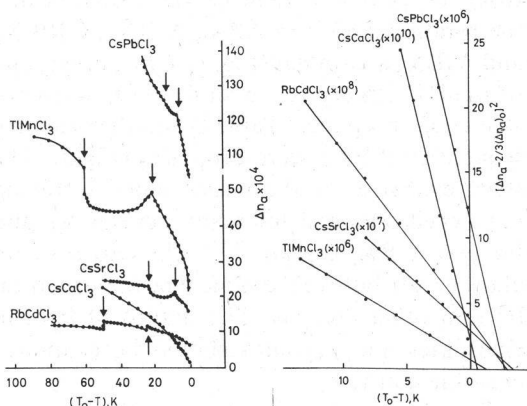where.[11] It is given for two independent PT

Fig. 1   **Fig. 2**

Fig. 1.   Temperature changes of the birefringence Δn_a in
some ABCl$_3$-Perovskites.

Fig. 2.   The dependences of $[\Delta n_a - 2/3(\Delta n_a)_0]^2$ vs
$(T_0 - T)$ in ABCl$_3$ crystals.

Table I. The thermodynamical characteristics of $O_h^1 \to G_1$ PTs in ABX_3 crystals.

Crystal	T_1 (K)	T_2 (K)	T_3 (K)	$(\Delta n_a)_0 \cdot 10^4$	$q \cdot 10^4$ (grade^{-2})	$(B/C) \cdot 10^{17}$ (cm^2)	$(B/A_T) \cdot 10^{-18}$ (cm$^{-2} \cdot$ K)	$T_0 - T_c$ (K)	$T_{cr} - T_0$ (K)	Reference
CsPbCl$_3$	320	315	310	104	3.18	−0.9	−3.5	7.8	2.6	this work
						−0.26	−7.5	12.8	4.3	(16)
TlMnCl$_3$	296	275	234	24	0.66	−0.9	−1.7	3.9	1.3	this work
						−0.8	−1.6	8.8	2.9	(15)
CsSrCl$_3$	385	377	362	16	0.60	−1.3	−2.9	9.6	3.1	this work
RbCdCl$_3$	385	361	339	5	0.40	−0.25	−10.9	6.8	2.2	this work
CsCaCl$_3$	95			0.4	0.6	−0.03	−16	1.2	0.4	this work
KMnF$_3$	186	95		1.7	0.62	−0.1	−0.4	6.1	0.03	(3)
RbCaF$_3$	196			2.2	0.6	−0.15	−0.27	0.1	0.03	(18, 19)

parameters η_i and ξ_i ($i = 1, 2, 3$) associated with BX_6 tilts at the condensation of the modes M_3 and R_{25}. The experimental data lack for the analysis of the PT sequence. Therefore it is reasonable to restrict the consideration to $O_h^1 \to G_1$ PTs.

If $O_h^1 \to G_1$ PT to tetragonal phase (for example, into D_{4h}^5 or D_{4h}^{18} space group)[2] takes place, one component of the PT parameter η_3 or ξ_3 is not equal to zero. Then the thermodynamical potential[11] of $O_h^1 \to D_{4h}^5$ PT without the cross-terms of η_3 and the mechanical strain can be written as

$$\phi = \phi_0 + A_T(T - T_c)\eta^2 + B\eta^4 + C\eta^6 + \ldots \quad (1)$$

Here $\eta \equiv \eta_3$, A_T, B, C are the potential constants, T_c—the Curie temperature. The last term is included into the expansion because of the possibility of PTs close to critical point. The temperature dependence of η near the first order PT ($B < 0$) can be found by usual way

$$\eta^2 = 2/3\eta_0^2 + 1/3\eta_0^2 \\ \times [1 + 3(T_0 - T)(T_0 - T_c)^{-1}]^{1/2} \quad (2)$$

where η_0-the jump of η at the transition point T_0; η_0 and $(T_0 - T_c)$ are determined by the relations:

$$\eta_0^2 = -(B/2C), \quad (T_0 - T_c) = B^2/4A_TC.^{6,12}$$

The birefringence changes in G_1 phase are due to PT parameter η and the spontaneous strain x_s[8]

$$\Delta n_a = n_b - n_c = 1/2 n_0^3 [D\eta^2 + (p_{11} - p_{12})x_s] \quad (3)$$

Here n_0-refraction index; p_{11}, p_{12}-elastooptic constants of O_h^1 phase. At the small tilts of BX_6 octahedra it can be approximately put: $\eta \approx (a/2)\varphi$ and $x_s = (c/a) - 1 \approx \varphi^2/2$,[13] where a and c-unit cell parameters, φ-tilt angle. Then the expression (3) can be transformed to

$$\Delta n_a = n_b - n_c = 1/4 n_0^3 \left[D\frac{a^2}{2} + (p_{11} - p_{12}) \right]\varphi^2 \\ = 1/4 n_0^3 q \varphi^2 \quad (4)$$

The equation (4) describes the birefringence changes at the structural PTs in ABX_3 perovskites. It is similar to the expression for the spontaneous electro-optical effect of ABO_3 ferroelectrics.[5] The coefficient q was determined

Table II. The coefficients of the thermodynamical potential of ABX_3 crystals.

| Crystal	a (Å)	n_0^3	$\Delta C_p \cdot 10^{-7}$ (erg·cm^{-3}·K^{-1})	$A_T \cdot 10^{-22}$ (erg·cm^{-5}·K^{-1})	$B \cdot 10^{-40}$ (erg·cm^{-7})	$C \cdot 10^{-57}$ (erg·cm^{-9})	$\omega_k^2 \cdot 10^{3*}$ (cm^{-2})	Reference
CsPbCl$_3$	5.605	7.4	0.169	1.8	−6.3	7.0	2.4	(16)
				1.2	−9.0	34.0	2.9	this work
TlMnCl$_3$	5.25	7.3	0.098	0.56	−0.95	1.06	0.7	this work
				0.75	−1.7	1.1		this work
CsCaCl$_3$	5.396	4.1	0.118	19.8	−317.3	10576	23.9	this work
KMnF$_3$	4.190	3.04	1.444	3.1	−1.24	12.4	3.3	this work
				10.8	−95.0	700	11	(15)
RbMnCl$_3$	a = 7.16 c = 17.8	4.97	0.029	30.9	4500			this work

*) For $T - T_c = 40$ K
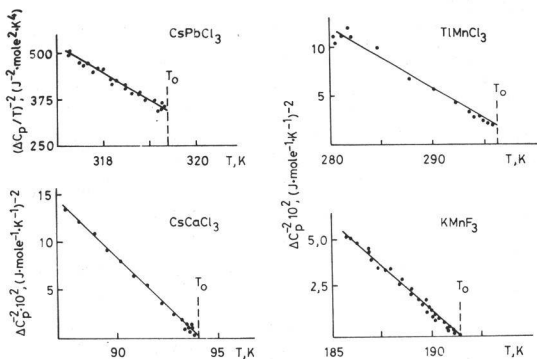
Fig. 3. Temperature dependences of the heat capacity in some ABX_3 crystals.

with help of corrected X-ray data.[14] It is nearly the same for all crystals under study, except $CsPbCl_3$ (Table I).

Taking in account $|\eta| \sim |\varphi|$ and equation (4) the temperature dependence of birefringence is determined by the equation (3) with the substitutions $\eta^2 \to (\Delta n_a)^2$ and $\eta_0^2 \to (\Delta n_a)_0^2$. The birefringence jump at T_0 is equal to $(\Delta n_2)_0 = 1/4n_0^3 \cdot q\varphi_0^2$. By plotting the experimental data of $[\Delta n_a - 2/3(\Delta n_a)_0]^2$ versus $(T_0 - T)$ (Fig. 2) the values B/C, B/A_T and $(T_0 - T_c)$ were found (Table I). We can conclude that the thermodynamical theory satisfactorily describes the behaviour of crystals in G_1-phases. The nearness of PT to the critical point can be estimated by means of criterion $T_{cr} - T_0 = B^2/12A_T C$.[15] The PTs in $ABCl_3$ crystals are rather close to the critical point (Table I). It seems that it is the reason why the β-index deviates from the classical value $\beta = 0.5$.[3]

Numerical values of the potential constants obtained from the birefringence measurements are in agreement with those for $CsPbCl_3$ and $TlMnCl_3$ which are evaluated from the elasticity[16] and heat capacity data.[15] To calculate A_T, B and C values it is necessary to use the birefringence data and for example heat capacity ones. The data of ref. (15) were used.

The theory[6] also explains satisfactorily the properties of some ABF_3 perovskites, for example, $KMnF_3$ and $RbCaF_3$.[3, 4, 17, 18] The esti-

mations showed that the PTs of these crystals are more close to the critical point than those of $ABCl_3$ (Table I).

$RbMnCl_3$ has the structure related to perovskite. PT $D_{6h}^4 \to C_{2h}^2$ of the second order takes place at 272 K without the change of the unit cell.[19] The thermodynamical evaluations for $RbMnCl_3$ were also made and the results are shown in Table I.

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